

USING WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE
SPECTROMETRY TO MEASURE CATION SEQUESTRATION
BY WOMBAT TIRE-DERIVED PARTICLES

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INTRODUCTION: Because wavelength-dispersive x-ray fluorescence (WDXRF) spectrometry may be utilized to examine a variety of condensed phase samples, it has been helpful to this group in our development of a tire processing technique called the WOMBAT -- for analysis of the black graining powder which is one product of the WOMBAT process. This powder, formed by degradation of the styrene-butadiene rubber in the tire, is dispersed in the mixed solvent prior to removal from the WOMBAT reactor and is separated from the mixed solvent by filtration and drying. This tire-derived powder is an important process component.

To a first approximation, the intensity of an analyte peak in the WDXRF spectrum of a multi-component sample is approximately proportional to the abundance of that analyte. This group has used a series of mixtures of solid state materials to approximate the abundances of key analytes (zinc, sulfur, and iron) in tires and in the tire-derived powders that have been produced from chemical degradation of the tires. The WDXRF spectrum of the WOMBAT solid tire-derived solid (TDP) contains a sulfur K_{α} peak which is smaller than the sulfur K_{α} peak (at 5.37 Å) in the untreated tire. The WDXRF spectrum of the black TDP powder is presented in Figure 1. The small zinc K_{α} peak (at 1.44 Å) in the WDXRF spectra of the tire-derived powder, when compared to the corresponding peak in the WDXRF spectrum of the untreated tire, indicates to ca. 95% of the zinc has been removed from the tire during our chemical processing. Using the same analysis procedure, the sulfur abundance is reduced by ca. 35% in the transition from the untreated tire to the TDP. The sulfur reduction produces a material, i.e., the TDP, which is a low polluting solid state fuel. However, the WDXRF spectrum of the TDP contains large iron peaks (K_{α} and K_{β} at 1.77 Å and at 1.94 Å, respectively) that are not present at such intensities in the WDXRF of the untreated SBR from the tire. The intensity of the Fe peaks in the WDXRF spectra of TDP is related to the length of time the TDP is allowed to remain in the reactor. The presence of the large iron peaks is consistent with the following reaction sequences:

- dissolution of iron from the steel belts into the reactor solution, and
- *in vivo* sequestration of the iron from the reaction solution by the TDP.

In order to determine if the TDP produced by the WOMBAT process is effective in sequestering other metal ions from solutions, small aliquots of the TDP have been introduced into aqueous solutions containing selected dissolved metal salts. Our results are presented below.

EXPERIMENTAL PROCEDURE: Five grams of TDP were dispersed into 100 ml of 0.1 molar aqueous solutions containing several reagent metal salts. After allowing the TDP to equilibrate, the TDP was separated from the aqueous solution by filtration, and then dried in a convective oven.

Each dried sample of treated TDP was then split into two parts. Part one was mounted onto a sample holder, and a WDXRF spectrum was obtained. Part two of each treated TDP sample was thoroughly washed with water and then recovered by filtration, dried, and mounted onto a sample holder. A schematic of the process is presented in Figure 2.

A wavelength dispersive x-ray fluorescence (WDXRF) spectrum of each sample was obtained using a Rigaku S-Max spectrometer equipped with an end-centered rhodium x-ray tube to cause elemental excitations and a graphite monochromator to disperse the secondary Xrays emitted by each sample during de-excitation. Each spectrum was obtained by collecting intensities for 4 second intervals between the angles of $2\theta = 8.00^\circ$ and $2\theta = 140.00^\circ$ at increments of $\Delta 2\theta = 0.05^\circ$.

RESULTS: Shown in Figures 3-6 are the WDXRF spectra of the TDP recovered from the

aqueous solution containing Cu^{+2} [Cu-TDP], from the aqueous solution containing Cr^{+3} [Cr-TDP], from the aqueous solution containing Hg^{+2} [Hg-TDP], and from the aqueous solution containing Pb^{+2} [Pb-TDP], respectively. In all of these WDXRF spectra, the zinc peak characteristic of the TDP has become too low to be detected, but the iron peaks are clearly discernible and only slightly less intense than in the WDXRF spectrum of the untreated TDP. The peak(s) due to the metal ions sequestered onto the TDP are labeled in each figure.

Thus, the spectra obtained may be explained in the following manner:

- Large copper peaks, K_β at 1.39 Å and K_α at 1.54 Å, appear in this WDXRF spectrum.
- The L_β and L_α peaks due to mercury, at 1.05 Å and at 1.24 Å are quite large in the WDXRF spectrum of this sample.
- The L_β and L_α peaks for lead, at 0.98 Å and at 1.18 Å, are small but clearly discernible in that WDXRF spectrum.
- The K_α peak for chromium, at 2.25 Å, is small but discernible.

Based on qualitative evaluation of the metal ion peaks in these spectra, the spectra was be divided into two groups. In the spectrum of the copper-containing TDP and in the spectrum of the mercury-containing TDP, the analyte peaks are quite large. However, for the spectra of the lead-containing TDP and of the chromium-containing TDP, the analyte peaks are quite small.

In a sample containing several types of atoms, the K_α peak intensity for analyte A (at λ_A) is given by:

$$I_A(\lambda_A) = M(\lambda_A) \cdot \eta_A \cdot I_A(\lambda_A) \cdot \exp[-\{\mu_s(\lambda_{Rh}) + \mu_s(\lambda_A)\} \cdot t_s \cdot \rho_s]; \quad (1)$$

where $\mu_s(\lambda_{Rh})$ is the mass absorption coefficient of the sample for the rhodium Xrays, $\mu_s(\lambda_A)$ is the mass absorption of the sample for the secondary Xrays emitted by analyte A contained in the sample of average thickness is t_s and density ρ_s . The abundance of analyte A is given by η_A , and $I_A^*(\lambda_A)$ is the absorption-free intensity for a pure sample of analyte A. $M(\lambda_A)$ described the efficiency of the spectrometer in measuring intensity at wavelength λ_A . For similar samples (P and Q) containing analyte A, a ratio of intensities measured from the WDXRF spectra of sample P and of sample Q may be used to estimate differences in the abundance of analyte A; i.e.,

$$I_{A-P}(\lambda_A) / I_{A-Q}(\lambda_A) \approx \eta_{A-P} / \eta_{A-Q} \quad (2)$$

Shown in Figure 7 are the WDXRF spectra of the Cu-containing TDP before and after the thorough washing with distilled water. The intensity of the copper peaks is decreased by 75-80%. A smaller reduction in peak intensity is noted when the WDXRF spectra of the Hg-containing samples, prior to and after washing with distilled water, are compared (see Figure 8).

The group is attempting to develop methods for utilizing the intensities of the "marker" peaks as the basis for making the matrix absorption effects to the intensities of the analyte peaks, so that the latter may be used to provide realistic measurements of the analytes sequestered onto the WOMBAT TDP.

CONCLUSIONS. The WOMBAT TDP sequesters several metal ions from aqueous solutions. Of these ion, both copper(II) and mercury(II) may be removed from the TDP by washing with distilled water.

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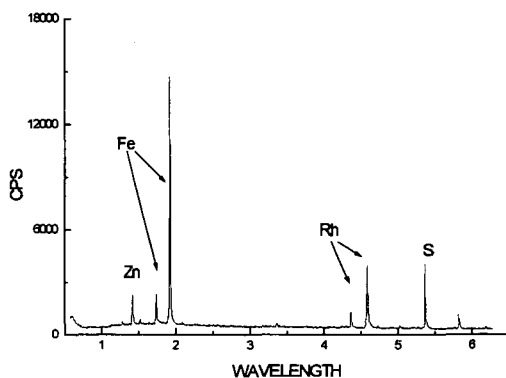


Figure 1. WDXRF spectrum of the WOMBAT TDP.

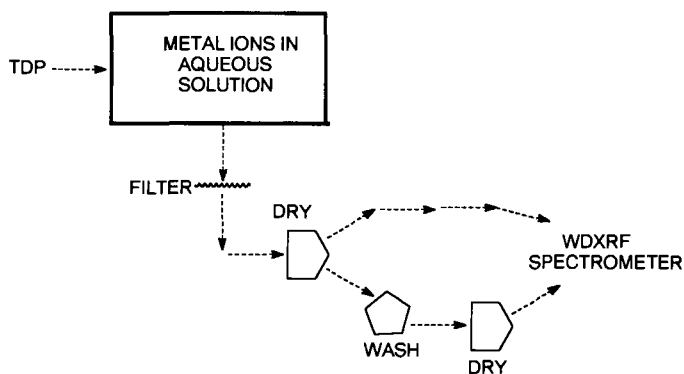


Figure 2. Schematic of the sequestering-washing experiments using WOMBAT TDP.

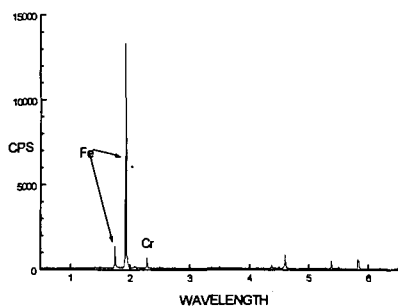


Figure 3. WDXRF spectrum of Cr-TDP.

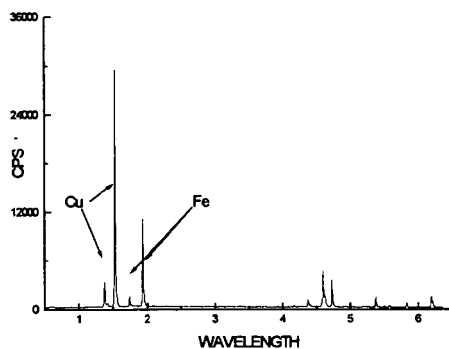


Figure 4. WDXRF spectrum of Cu-TDP.

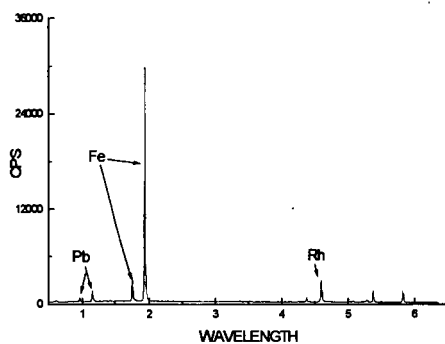


Figure 5. WDXRF spectrum of Pb-TDP.

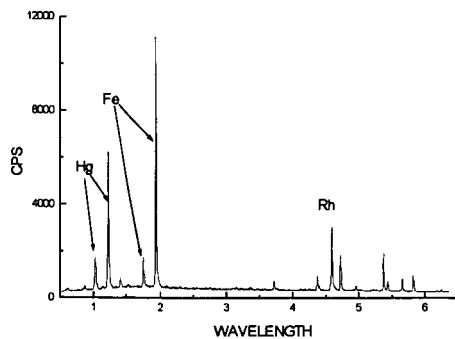


Figure 6. WDXRF spectrum of the Hg-TDP.

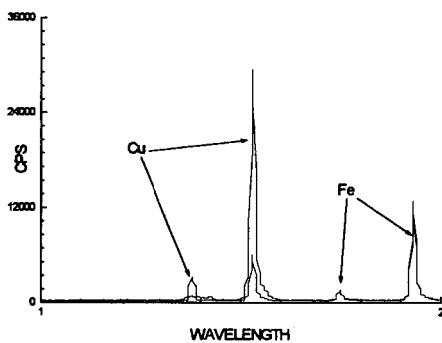


Figure 7. Comparison of the WDXRF spectra of Cu-TDP prior to and after washing with water.

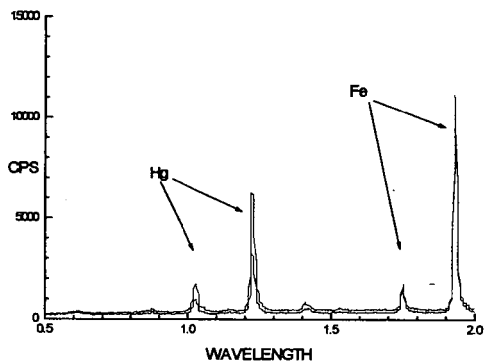


Figure 8. Comparison of the WDXRF spectra of Hg-TDP prior to and after washing with water.